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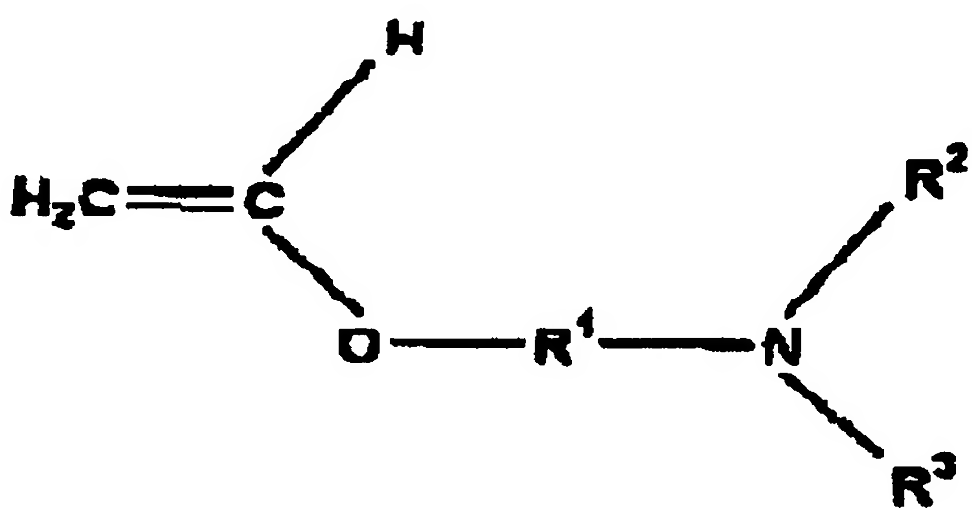
(54) Titre : COPOLYMERES D'ETHER D'AMINOPROPYLVINYLE
(54) Title: COPOLYMERS OF AMINOPROPYL VINYL ETHER



(I)

(57) Abrégé/Abstract:
The invention relates to antimicrobial polymers which can be obtained by copolymerizing vinyl ethers of general formula (I), especially 3-aminopropyl vinyl ethers, with additional aliphatically unsaturated monomers, and to a method for the production thereof. The polymers can also be produced by graft copolymerizing a substrate, whereby a covalently bound coating is obtained on the surface of the substrate. The antimicrobial polymers can be used as a microbicide coating, among other things, on hygiene articles or in the field of medicine, as well as in paints or protective paint coatings.

Abstract

The invention relates to antimicrobial polymers which can be obtained by copolymerizing vinyl ethers of general formula (I), especially 3-aminopropyl vinyl ethers, with additional aliphatically unsaturated monomers, and to a method for the production thereof. The polymers can also be produced by graft copolymerizing a substrate, whereby a covalently bound coating is obtained on the surface of the substrate. The antimicrobial polymers can be used as a microbicide coating, among other things, on hygiene articles or in the field of medicine, as well as in paints or protective paint coatings.

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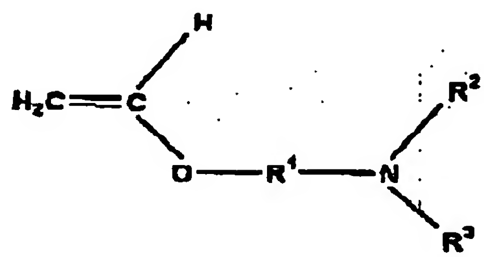
What is claimed is:

1. An antimicrobial copolymer, obtainable by copolymerizing a vinyl ether of the general formula



where R^1 is a branched or unbranched hydrocarbon radical having from 1 to 5 carbon atoms, and
R^2 is H, and
R^3 is H or a branched or unbranched hydrocarbon radical having from 1 to 5 carbon atoms,

with at least one aliphatically unsaturated monomer.

2. An antimicrobial polymer as claimed in claim 1, wherein the vinyl ether used comprises 3-aminopropyl vinyl ether.

3. An antimicrobial polymer as claimed in claim 1 or 2, wherein the aliphatically unsaturated monomers are methacrylic acid compounds.

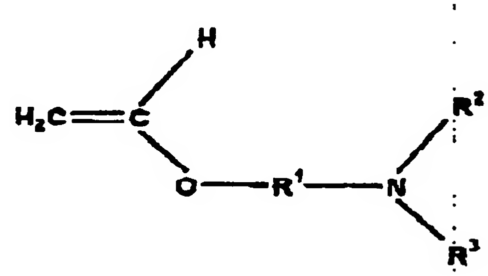
4. An antimicrobial polymer as claimed in claim 1 or 2,

wherein the aliphatically unsaturated monomers are acrylic acid compounds.

5. An antimicrobial polymer as claimed in claim 1 or 2, wherein the aliphatically unsaturated monomers used are methyl methacrylate, ethyl methacrylate, butyl methacrylate, tert-butyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, tert-butyl acrylate, tert-butylaminoethyl esters, 2-diethylaminoethyl methacrylate, 2 diethylaminoethyl vinyl ether, N-3-dimethylaminopropylmethacrylamide, 3-methacryloylaminopropyltrimethylammonium chloride, 2-methacryloyloxyethyltrimethylammonium chloride or 2-methacryloyloxyethyltrimethylammonium methosulfate.

6. An antimicrobial polymer as claimed in any one of claims 1 to 5, wherein the copolymerization is carried out on a substrate.

7. An antimicrobial coating of a substrate, wherein vinyl ethers of the general formula



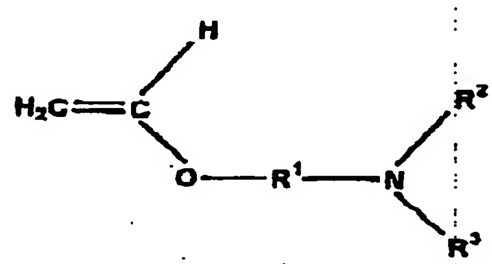
where R^1 is a branched or unbranched hydrocarbon radical having from 1 to 5 carbon atoms, and
R^2 and R^3 are H or a branched or unbranched hydrocarbon radical having from 1 to 5 carbon atoms, where R^2 and R^3 may be identical or different,

are copolymerized in graft polymerization of a substrate.

8. An antimicrobial coating as claimed in claim 7, wherein
the substrate is activated prior to the graft polymerization by UV radiation, plasma treatment, corona treatment, flame treatment, ozonization, electrical discharge or γ-radiation.

9. An antimicrobial coating as claimed in claim 7, wherein
the substrate is activated, prior to the graft polymerization, by UV radiation with a photoinitiator.

10. A process for preparing antimicrobial copolymers, which comprises
copolymerizing a vinyl ether of the general formula



where R^1 is a branched or unbranched hydrocarbon radical having from 1 to 5 carbon atoms,
R^2 is H, and
R^3 is H or a branched or unbranched hydrocarbon radical having from 1 to 5 carbon atoms,

with at least one aliphatically unsaturated monomer.

11. The process as claimed in claim 10, wherein the vinyl ether used comprises 3-aminopropyl vinyl ether.

12. The process as claimed in claim 10 or 11, wherein the aliphatically unsaturated monomers are methacrylic acid compounds.

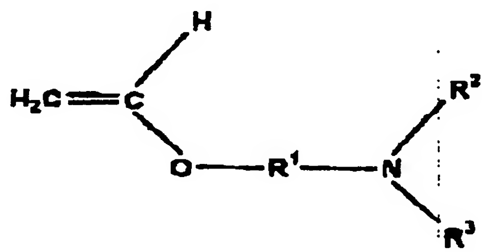
13. The process as claimed in claim 10 or 11, wherein the aliphatically unsaturated monomers are acrylic acid compounds.

14. The process as claimed in claim 10 or 11, wherein the aliphatically unsaturated monomers used are methyl methacrylate, ethyl methacrylate, butyl methacrylate, tert-butyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, tert-butyl acrylate, tert-butylaminoethyl esters, 2-diethylaminoethyl methacrylate, 2-diethylaminoethyl vinyl ether, N-3-dimethylaminopropylmethacrylamide, 3-methacryloylaminopropyltrimethylammonium chloride, 2-methacryloyloxyethyltrimethylammonium chloride or

2-methacryloyloxyethyltrimethylammonium methosulfate.

15. The process as claimed in any one of claims 10 to 14,
wherein
the copolymerization is carried out on a substrate.

16. A process for preparing an antimicrobial coating of a substrate,
which comprises
copolymerizing vinyl ethers of the general formula



where R^1 is a branched or unbranched hydrocarbon radical having from 1 to 5 carbon atoms, and R^2 and R^3 are H or a branched or unbranched hydrocarbon radical having from 1 to 5 carbon atoms, where R^2 and R^3 may be identical or different,

in graft polymerization of a substrate.

17. The process as claimed in claim 16,
wherein
the substrate is activated prior to the graft polymerization by UV radiation, plasma treatment, corona treatment, flame treatment, ozonization, electrical discharge or γ-radiation.

18. The process as claimed in claim 16, wherein the substrate is activated prior to the graft polymerization by UV radiation with a photoinitiator.

19. The use of the antimicrobial polymers as claimed in any of claims 1 to 9 for producing products with an antimicrobial coating of the polymer.

20. The use of the antimicrobial polymers as claimed in any one of claims 1 to 9 for producing medical items with an antimicrobial coating of the polymer.

21. The use of the antimicrobial polymers as claimed in any one of claims 1 to 9 for producing hygiene items with an antimicrobial coating of the polymer.

22. The use of the antimicrobial polymers as claimed in any one of claims 1 to 9 in surface coatings, protective paints or other coatings.

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Copolymers of aminopropyl vinyl ether

The invention relates to antimicrobial polymers obtained by copolymerizing aminofunctionalized vinyl ethers with other monomers. The invention further relates to a process for preparing these antimicrobial polymers, and to their use.

The invention further relates to antimicrobial polymers obtained by a graft copolymerization of aminofunctionalized vinyl ethers with other monomers on a substrate, and also to a process for the preparation of the graft copolymers, and to their use.

It is highly undesirable for bacteria to become established or to spread on the surfaces of pipelines, containers or packaging. Frequently, slime layers form and permit sharp rises in microbial populations, and these can lead to persistent impairment of the quality of water, drinks or foods, and even to spoilage of the product and harm to the health of consumers.

Bacteria must be kept away from all areas of life in which hygiene is important. This affects textiles for direct body contact, especially in the genital area, and for the care of the elderly and sick. Bacteria must also be kept away from surfaces of furniture and instruments in wards, especially in areas for intensive care and neonatal care, in hospitals, especially in areas for medical interventions, and in isolation wards for critical cases of infection, and also in toilets.

A current method of treating equipment, or the surfaces of furniture or textiles, to resist bacteria, either when this becomes necessary or else as a precautionary measure, is to use chemicals or solutions or mixtures of these which as disinfectants have fairly broad and general antimicrobial action. Chemical agents of this type act nonspecifically and are frequently themselves

toxic or irritant, or form degradation products which are hazardous to health. In addition, people frequently exhibit intolerance to these materials once they have become sensitized.

Another method to counteract surface spread of bacteria is to incorporate substances with antimicrobial action into a matrix.

tert-Butylaminoethyl methacrylate is a commercially available monomer in methacrylate chemistry and is used in particular as a hydrophilic constituent in copolymerizations. For example, EP-B 0 290 676 describes the use of various polyacrylates and polymethacrylates as a matrix for immobilizing bactericidal quaternary ammonium compounds.

In another technical sector US-A 4 532 269 discloses a terpolymer of butyl methacrylate, tributyltin methacrylate and tert-butylaminoethyl methacrylate. This polymer is used as an antimicrobial paint for ships: the hydrophilic tert-butylaminoethyl methacrylate promotes gradual erosion of the polymer, thus liberating the highly toxic tributyltin methacrylate as antimicrobial agent.

In these applications the copolymer prepared using aminomethacrylates is merely a matrix or carrier substance for added microbicidal agents which can diffuse or migrate out of the carrier substance. Sooner or later, polymers of this type lose their effectiveness once the "minimal inhibitory concentration" (MIC) is no longer achieved on the surface.

European Patent Applications 0 862 858 and 0 862 859 have disclosed that homo- and copolymers of tert-butylaminoethyl methacrylate, a methacrylate having a secondary amino function, have inherent microbicidal

properties. To avoid undesirable resistance phenomena in the microbes, particularly bearing in mind the development of resistance by bacteria known from antibiotics research, systems developed in the future will also have to be based on novel compositions with improved effectiveness.

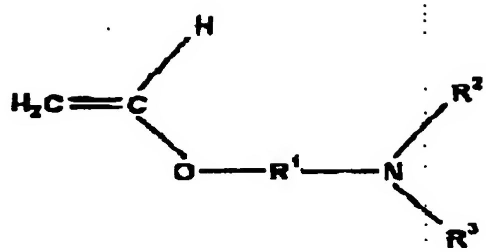
US 2 980 634 discloses antimicrobial polymers based on vinyl ethers and having a tertiary amino function. Those polymers may be quaternized before or after polymerization.

The object of the present invention is therefore to develop novel polymers having antimicrobial action which prevent the establishment and spread of bacteria on surfaces.

Surprisingly, it has now been found that copolymerizing aminofunctionalized vinyl ethers with aliphatically unsaturated monomers and, respectively, a graft copolymerization of these components on a substrate gives polymers with a surface which is durably microbicidal, resists solvents and physical stresses and does not exhibit migration. This means that there is no need for other biocides to be used.

3-Aminopropyl vinyl ether is a commercially available product whose preparation can be found, for example, in the European Patent Application 0 514 710. It is used, inter alia, as an additive for photoresist systems, described, for example, in US 5648194, or as an element in the structure of adhesion promoters in specific urethane-silanes, described, for example, in US 5384342. The use of compounds of this type in antimicrobial polymers is not known.

The present invention therefore provides antimicrobial copolymers which are obtained by copolymerizing a vinyl ether of the general formula



where R^1 is a branched or unbranched hydrocarbon radical having from 1 to 5 carbon atoms,
R^2 is H, and
R^3 is H or a branched or unbranched hydrocarbon radical having from 1 to 5 carbon atoms,

with at least one aliphatically unsaturated monomer.

The proportion of vinyl ethers in the reaction mixture should be from 5 to 98 mol%, preferably from 30 to 90 mol%, particularly preferably from 50 to 98 mol%, based on the total of the monomers, in order to obtain sufficient antimicrobial action from the polymer.

The aliphatically unsaturated monomers used may be any monomers which enter into copolymerization with the vinyl ethers of the general formula. Examples of suitable monomers are acrylates or methacrylates, such as acrylic acid, tert-butyl methacrylate or methyl methacrylate, styrene, vinyl chloride, vinyl ethers, acrylamides, acrylonitriles, olefins (ethylene, propylene, butylene or isobutylene), allyl compounds, vinyl ketones, vinyl acetic acid, vinyl acetate or vinyl esters, in particular, for example, methyl methacrylate, ethyl methacrylate, butyl methacrylate, tert-butyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, tert-butyl acrylate, tert-butylaminoethyl esters, 2-diethylaminoethyl methacrylate, 2-diethylaminoethyl vinyl ether, N-3-diethylaminopropylmethacrylamide, 3-methacryloyl-

aminopropyltrimethylammonium chloride, 2-methacryloyloxyethyltrimethylammonium chloride or 2-methacryloyloxyethyltrimethylammonium methosulfate.

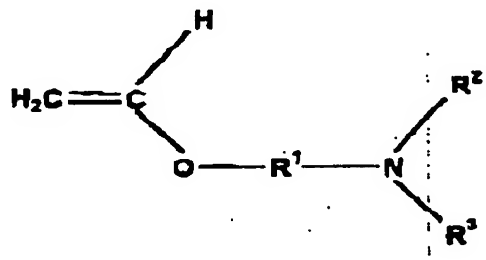
The aliphatically unsaturated monomers are preferably acrylic acid compounds or methacrylic acid compounds, and the vinyl ethers of the general formula are preferably 3-aminopropyl vinyl ether.

The novel antimicrobial copolymers may be obtained by copolymerizing vinyl ethers of the general formula, in particular 3-aminopropyl vinyl ethers with one or more aliphatically unsaturated monomers. The polymerization is usefully a free-radical polymerization using a free-radical initiator or induced by radiation. Typical procedures are described in the examples.

The novel antimicrobial copolymers may also be obtained by copolymerizing vinyl ethers of the general formula, in particular 3-aminopropyl vinyl ether with at least one aliphatically unsaturated monomer on a substrate. This gives a physisorbed coating of the antimicrobial copolymer on the substrate.

Suitable substrate materials are especially any of the polymeric plastics, such as polyurethanes, polyamides, polyesters or polyethers, polyether block amides, polystyrene, polyvinyl chloride, polycarbonates, polyorganosiloxanes, polyolefins, polysulfones, polyisoprene, polychloroprene, polytetrafluoroethylene (PTFE) or corresponding copolymers or blends, or else naturally occurring or synthetic rubbers, with or without radiation-sensitive groups. The novel process may also be used on the surfaces of objects made from metal, from glass or from wood and surface-coated or otherwise coated with plastic.

In another embodiment of the present invention the copolymers may be prepared by a graft polymerization of a substrate with vinyl ethers of the general formula



where R^1 is a branched or unbranched hydrocarbon radical having from 1 to 5 carbon atoms, and R^2 and R^3 are H or a branched or unbranched hydrocarbon radical having from 1 to 5 carbon atoms, where R^2 and R^3 may be identical or different,

in particular with 3-aminopropyl vinyl ether, and with at least one aliphatically unsaturated monomer. The grafting of the substrate allows covalent linking of the antimicrobial copolymer to the substrate. Substrates which may be used are any polymeric material, such as the plastics mentioned above.

Prior to the graft copolymerization, the surfaces of the substrate may be activated by a variety of methods. Any standard method for activating polymer surfaces may be used here, for example the substrate may be activated prior to the graft polymerization by UV radiation, plasma treatment, corona treatment, flame treatment, ozonization, electrical discharge or γ-radiation. The surfaces are usefully freed in advance in a known manner from oils, fats or other contamination, using a solvent.

The substrates may be activated using UV radiation in the wavelength range from 170 to 400 nm, preferably

from 170 to 250 nm. An example of a suitable radiation source is a Noblelight UV excimer apparatus from HERAEUS, Hanau, Germany. However, mercury vapor lamps are also suitable for substrate activation as long as they emit substantial proportions of radiation in the abovementioned ranges. The exposure time is generally from 0.1 seconds to 20 minutes, preferably from 1 second to 10 minutes.

The activation of the substrate with UV radiation prior to the graft polymerization may also be done using an additional photosensitizer. For this, the photosensitizer, such as benzophenone, is applied to the substrate surface and irradiated. A mercury vapor lamp may again be used here, with exposure times of from 0.1 second to 20 minutes, preferably from 1 second to 10 minutes.

According to the invention, the activation may also be achieved by plasma treatment using an RF or microwave plasma (Hexagon, Technics Plasma, 85551 Kirchheim, Germany) in air, nitrogen or argon atmospheres. The exposure times are generally from 2 seconds to 30 minutes, preferably from 5 seconds to 10 minutes. The energy supplied in the case of laboratory devices is from 100 to 500 W, preferably from 200 to 300 W.

Corona devices (SOFTAL, Hamburg, Germany) may also be used for activation. The exposure times in this case are generally from 1 to 10 minutes, preferably from 1 to 60 seconds.

Activation by electrical discharge, electron beam or γ-radiation (e.g. from a cobalt 60 source), and also ozonization, allows short exposure times, generally from 0.1 to 60 seconds.

Substrate surfaces may also be activated by flame treatment. Suitable devices, in particular those with a

barrier flame front, can readily be constructed or, for example, purchased from ARCOTEC, 71297 Mönsheim, Germany. They may be operated using hydrocarbons or hydrogen as combustion gas. In all cases it is necessary to avoid damage to the substrate by overheating, and this can readily be ensured if the surface of the substrate facing away from the flame treatment side is in intimate contact with a cooled metal surface. Activation by flame treatment is therefore restricted to relatively thin, sheet-like substrates. The exposure times are generally from 0.1 second to 1 minute, preferably from 0.5 to 2 seconds. The flames are exclusively nonluminous, and the distances between the substrate surfaces and the outer side of the flame front are from 0.2 to 5 cm, preferably from 0.5 to 2 cm.

The substrate surfaces activated in this way are coated by known methods, such as dipping, spraying or spreading, with vinyl ethers of the general formula (component I), in particular with 3-aminopropyl vinyl ether, and with one or more aliphatically unsaturated monomers (component II), in solution if desired. Solvents which have proven useful are water and water/ethanol mixtures, but other solvents may also be used as long as they are sufficiently capable of dissolving the monomers and give good wetting of the substrate surfaces. Solutions with monomer contents of from 1 to 10% by weight, for example about 5% by weight, have proven successful in practice and generally give, in a single pass, coherent coatings which cover the substrate surface and have thicknesses which can be more than 0.1 µm.

The graft copolymerization of the monomers applied to the activated surfaces may usefully be initiated by radiation in the short-wave segment of the visible range or in the long-wave segment of the UV range of electromagnetic radiation. For example, the radiation

from a UV excimer of wavelengths from 250 to 500 nm, preferably from 290 to 320 nm, is very suitable. Mercury vapor lamps are also suitable here as long as they have substantial proportions of radiation in the abovementioned ranges. The exposure times are generally from 10 seconds to 30 minutes, preferably from 2 to 15 minutes.

A graft copolymerization of the novel comonomer compounds can also be achieved by a process described in European Patent Application 0 872 512 and based on a graft polymerization of monomer molecules and initiator molecules incorporated by swelling. The monomer used for the swelling may be component II.

Even without grafting onto a substrate surface, the novel antimicrobial copolymers of vinyl ethers of the general formula (component I), in particular 3-aminopropyl vinyl ether with at least one aliphatically unsaturated monomer (component II) show microbicidal or antimicrobial behaviour. Another embodiment of the present invention consists in carrying out the copolymerization of components I and II on a substrate.

The components may be in solution when applied to the substrate. Examples of suitable solvents are water, ethanol, methanol, methyl ethyl ketone, diethyl ether, dioxane, hexane, heptane, benzene, toluene, chloroform, dichloromethane, tetrahydrofuran and acetonitrile. It is also possible to use component II as solvent for component I.

The novel antimicrobial copolymers may also be used directly, i.e. not by polymerizing the components on a substrate but as an antimicrobial coating. Suitable coating methods are application of the copolymers in solution or as a melt.

The solution of the novel polymers may be applied to the substrates by dipping, spraying or painting, for example.

If the novel polymers are used directly on the substrate surface without grafting, conventional free-radical initiators may be added.

Examples of initiators which may be used in the preparation of the novel copolymers are, inter alia, azonitriles, alkyl peroxides, hydroperoxides, acyl peroxides, peroxoketones, peresters, peroxocarbonates, peroxodisulfate, persulfate and any of the usual photoinitiators, such as acetophenones, α-hydroxyketones, dimethylketals and benzophenone. The polymerization may also be initiated thermally or, as already stated, by electromagnetic radiation, such as UV light or γ-radiation.

The novel antimicrobial polymers may also be used as components for formulating inks, paints or other surface coatings.

Use of the modified polymer substrates

The present invention also provides the use of the novel antimicrobial polymers to produce antimicrobially active products, and the products per se which are produced in this way. The products may comprise polymer substrates modified according to the invention or consist of these. Products of this type are preferably based on polyamides, polyurethanes, polyether block amides, polyesteramides or -imides, PVC, polyolefins, silicones, polysiloxanes, polymethacrylate or polyterephthalates which are surface-modified using novel polymers.

Examples of antimicrobially active products of this type are in particular machine parts for food processing, components in air-conditioning systems,

roofing, items for bathroom and toilet use, kitchen items, components of sanitary equipment, components of cages or houses for animals, recreational products for children, components of water systems, food packaging, operator units (touch panels) of devices, and contact lenses.

The novel copolymers or graft copolymers may be used anywhere where importance is placed on surfaces with release properties or surfaces which are very free from bacteria, i.e. microbicidal. Examples of application of the novel copolymers or graft polymers are in particular surface coatings, protective paints and other coatings in the following sectors:

- Marine: Boat hulls, docks, buoys, drilling platforms, ballast water tanks
- Construction: Roofing, basements, walls, facades, greenhouses, sun protection, garden fencing, wood protection
- Sanitary: Public conveniences, bathrooms, shower curtains, toilet items, swimming pool, sauna, jointing, sealing compounds
- Requisites for daily life: Machines, kitchen, kitchen items, sponge pads, recreational products for children, food packaging, milk processing, drinking water systems, cosmetics
- Machine parts: Air-conditioning systems, ion exchangers, process water, solar-powered units, heat exchangers, bioreactors, membranes
- Medical technology: Contact lenses, diapers, membranes, implants
- Consumer articles: Automobile seats, clothing (socks, sports clothing), hospital equipment, door handles, telephone handsets, public conveyances, animal cages, cash registers, wall-to-wall carpets, wallpapers.

The present invention also provides for the use of the novel polymer substrates, whose surfaces have been modified using novel polymers or processes, for producing hygiene products or items in medical technology. That which has been said above concerning preferred materials applies correspondingly. Examples of hygiene products of this type are toothbrushes, toilet seats, combs and packaging materials. The term hygiene item also includes other objects which may come into contact with a large number of people, such as telephone handsets, stair rails, door handles, window catches, and grab straps and grab handles in public conveyances. Examples of items in medical technology are catheters, tubing, protective or backing films and also surgical instruments.

The following examples are given in order to describe the present invention in greater detail, but are not intended to limit its scope as set out in the patent claims.

Example 1:

6 g of 3-aminopropyl vinyl ether (Aldrich), 6 g of methyl methacrylate (Aldrich) and 60 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.15 g of azobisisobutyronitrile dissolved in 4 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is stirred into 0.5 l of deionized water, whereupon the polymeric product precipitates. After filtering off the product, the filter cake is washed with 100 ml of deionized water to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C.

Example 1a:

0.05 g of the product from Example 1 is shaken in 20 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time Staphylococcus aureus microbes are no longer detectable.

Example 1b:

0.05 g of the product from Example 1 is shaken in 20 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^2.

Example 2:

6 g of 3-aminopropyl vinyl ether (Aldrich), 6 g of butyl methacrylate (Aldrich) and 60 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.15 g of azobisisobutyronitrile dissolved in 4 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is stirred into 0.5 l of deionized water, whereupon the polymeric product precipitates. After filtering off the product, the filter cake is washed with 100 ml of deionized water to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C.

Example 2a:

0.05 g of the product from Example 2 is shaken in 20 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed, and the

number of microbes in the test mixture is determined. After expiry of this time Staphylococcus aureus microbes are no longer detectable.

Example 2b:

0.05 g of the product from Example 2 is shaken in 20 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^2.

Example 3:

6 g of 3-aminopropyl vinyl ether (Aldrich), 6 g of 2-diethylaminoethyl methacrylate (Aldrich) and 60 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.15 g of azobisisobutyronitrile dissolved in 4 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is stirred into 0.5 l of deionized water, whereupon the polymeric product precipitates. After filtering off the product, the filter cake is washed with 100 ml of deionized water to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C.

Example 3a:

0.05 g of the product from Example 3 is shaken in 20 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^2.

Example 3b:

0.05 g of the product from Example 3 is shaken in 20 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^2.

Example 4:

6 g of 3-aminopropyl vinyl ether (Aldrich), 6 g of tert-butyl methacrylate (Aldrich) and 60 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.15 g of azobisisobutyronitrile dissolved in 4 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is stirred into 0.5 l of deionized water, whereupon the polymeric product precipitates. After filtering off the product, the filter cake is washed with 100 ml of deionized water to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C.

Example 4a:

0.05 g of the product from Example 4 is shaken in 20 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time Staphylococcus aureus microbes are no longer detectable.

Example 4b:

0.05 g of the product from Example 4 is shaken in 20 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed, and the

number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^2.

Example 5:

A nylon 12 film is exposed for 2 minutes at a pressure of 1 mbar to 172 nm radiation from a Heraeus excimer source. The film activated in this way is placed into an irradiator under an inert gas and secured. Under a counterstream of inert gas, the film is then covered with 20 ml of a mixture of 6 g of 3 aminopropyl vinyl ether (Aldrich), 6 g of butyl methacrylate (Aldrich) and 60 g of ethanol. The irradiation chamber is sealed and placed at a distance of 10 cm from a Heraeus excimer source emitting at wavelength 308 nm. Irradiation is begun and continues for 15 minutes. The film is then removed and rinsed with 30 ml of ethanol. The film is then dried for 12 hours at 50°C in vacuo. The film is then extracted in water for 5 times 6 hours at 30°C, then dried for 12 hours at 50°C.

The reverse side of the film is then treated in the same way, so that the nylon film finally obtained has been coated on both sides with grafted polymer.

Example 5a:

A piece of coated film from Example 5 (5 x 4 cm) is shaken in 30 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed and the number of microbes in the test mixture is determined. After expiry of this time Staphylococcus aureus microbes are no longer detectable.

Example 5b:

A piece of coated film from Example 5 (5 x 4 cm) is shaken in 30 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is

removed and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^4.

Example 6:

A nylon-12 film is exposed for 2 minutes at a pressure of 1 mbar to 172 nm radiation from a Heraeus excimer source. The film activated in this way is placed into an irradiator under an inert gas and secured. Under a counterstream of inert gas, the film is then covered with 20 ml of a mixture of 6 g of 3-aminopropyl vinyl ether (Aldrich), 4 g of tert-butyl methacrylate (Aldrich) and 60 g of ethanol. The irradiation chamber is sealed and placed at a distance of 10 cm from a Heraeus excimer source emitting at wavelength 308 nm. Irradiation is begun and continues for 15 minutes. The film is then removed and rinsed with 30 ml of ethanol. The film is then dried for 12 hours at 50°C in vacuo. The film is then extracted in water for 5 times 6 hours at 30°C, then dried for 12 hours at 50°C.

The reverse side of the film is then treated in the same way, so that the nylon film finally obtained has been coated on both sides with grafted polymer.

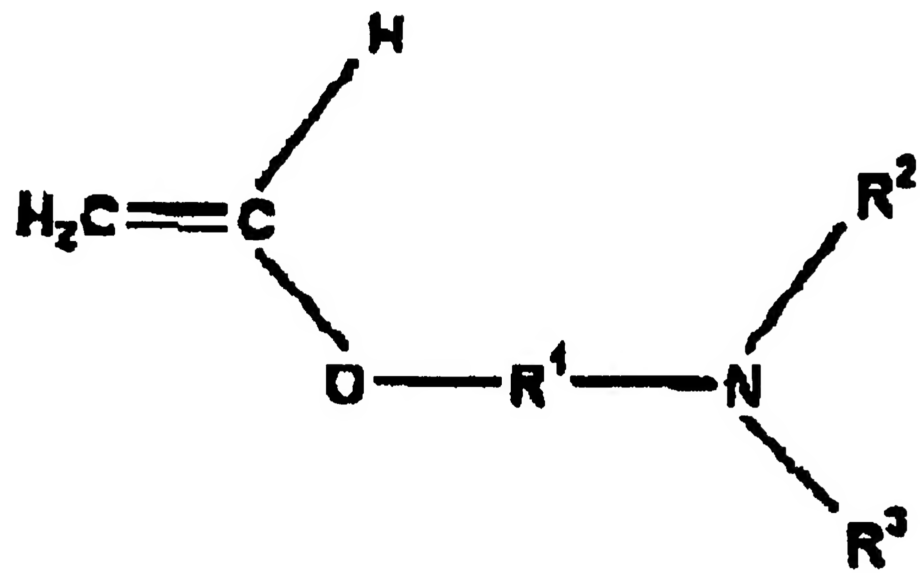
Example 6a:

A piece of coated film from Example 6 (5 x 4 cm) is shaken in 30 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed and the number of microbes in the test mixture is determined. After expiry of this time Staphylococcus aureus microbes are no longer detectable.

Example 6b:

A piece of coated film from Example 6 (5 x 4 cm) is shaken in 30 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is

removed and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^4.



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